SOLUBLE N-DOPING POLYMERS

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SOLUBLE N-DOPING POLYMERS

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CHAPTER 1

INTRODUCTION

Background of Electroactive Polymers

When one imagines a conducting material the first images that come to mind are probably copper, aluminum and generally something that is metallic in nature. In years to come this may not be the case. In 2000 Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa won the Nobel Prize in chemistry for their 1977 discovery that the oxidation of polyacetylene films with chlorine, iodine or bromine vapor caused them to have a conductivity 10⁹ times that of their un-doped form. ¹ Since this realization, much research has been devoted to synthesizing, characterizing and developing applications for various electroactive polymers (EAPs).

Common Electroactive Polymers

Some of the more common electroactive polymers are polyacetylene, poly(paraphenylene) (PPP), polypyrrole (PPy), polythiophene (PT), poly(phenylene vinylene) (PPV), and polyaniline (PANI) (see Figure 1).



Figure 1. Common conducting polymers

Polyacetylene is by far the most simple in structure of these polymers. It is composed of alternating single and double bonds which may exist in a *cis*- or *trans*configuration. If a Ziegler-Natta catalyst is used in the polymerization process, highly oriented films in the *trans*- configuration are produced with a conductivity of 10⁴ S cm⁻¹.² PPP is a polymer made up of phenylene repeat units bonded at the *para* position. This polymer suffers from insolubility and thus poor processability, leading to its inability to be characterized. Various methods have been employed to synthesize this polymer, but PPP generally suffers from low molecular weight. PPP does however have high thermal stability, it can achieve a wide range of conductivities, and it has better resistance to corrosion when compared with PPy and PANI.³ Polypyrroles are made from pyrrole monomers attached at the 2 and 5 positions. PPy has a lower oxidation potential compared to other EAPs, due to the electron rich nitrogen. PPy also suffers from insolubility; modifications to the polymer have been attempted, but a loss of conductivity is seen when these solubilizing groups are added. In general, the conductivity of PPy is low $(10^{-11} \text{ S cm}^{-1})$ however it is dramatically improved when doped with iodine $(10^{-5} \text{ S} \text{ cm}^{-1})$.² Polythiophene is made up of repeat units of thiophene bonded at the 2 and 5 positions. Polythiophene and its derivatives form some of the most environmentally and thermally stable materials.⁴ They have been used in many applications including, optical devices, light emitting diodes (LEDs), antistatic coatings, batteries and many others.⁴ PPV is a polymer consisting of alternating phenyl and vinyl groups. It becomes conductive with the addition of electron donors or acceptors. Some of the dopants include iodine and sulfuric acid, the conductivities of PPV doped with these dopants range from 10^{-5} to 10^{-3} S cm⁻¹.⁵ PANI is a polymer composed of repeat units of aniline bonded on either side of the nitrogen. It exhibits high chemical stability and has a relatively low conductivity in the range of 10^{-2} S cm⁻¹.⁶ The conductivity can be improved however with molecular engineering or by mixing with organic and inorganic compounds to obtain conductive composites.⁶

Fundamentals of Electroactive Polymer Doping Processes

EAPs are intrinsically conducting polymers that are fully conjugated.⁷ The alternation of single and multiple bonds causes there to be delocalized electrons along the backbone, and provides a path for mobility of the electrons. In their un-doped form EAPs may be either semi-conducting or insulating. Once these EAPs are doped, their conductivity increases considerably. This "doping" is accomplished by redox processes (see Figure 2). When the polymer is reduced (n-doped), extra electrons are added to the polymer, and when the polymer is oxidized (p-doped) electrons are removed creating holes that neighboring electrons can fill and thus move the holes up and down the

backbone. A counter ion is needed in both cases to insure charge stability. Redox doping may be performed by electrical or electrochemical means and both reduction and oxidation are reversible processes.² While a polymer may be p-doped or n-doped; their ability to do either depends on the functional groups within the backbone. For instance, EAPs that contain electron donating and accepting groups are better able to stabilize an ndoped polymer.⁸ n-Doped polymers are also more unstable and highly susceptible to oxidation in ambient conditions.⁹



Figure 2. Scheme showing the processes of oxidative polymerization p-doping and n-doping

Band Gap

In small molecules there are discrete orbitals, but as conjugation increases there are so many orbitals of similar energy that they begin to blend together to form bands.¹⁰ The valence band is full of electrons (analogous to the highest occupied molecular orbital, or HOMO, in small molecules), while the conduction band is empty until the polymer is doped (analogous to the lowest unoccupied molecular orbital, or LUMO, in small molecules). The band gap (E_g) is the energy difference between the valence and conduction bands (see Figure 3). In order for an EAP to be able to conduct, it must be able to promote electrons from the valence band to the conduction band. Fully conjugated systems have lower band gaps than non-conjugated systems, because when an electron is removed from the valence band the subsequent positive charge is delocalized along the polymer backbone. The pi bonds also lead to a planar geometry which aids electron transport along the backbone. Due to hybridization of the orbitals, p-doping and n-doping further decrease the energy required to promote electrons by creating discrete new levels within the band gap.¹⁰



Figure 3. Conjugation causes discrete molecular orbitals to combine to form bands; as conjugation increases, the energy difference between vacant and occupied orbitals/bands (bandgap) decreases.²

Structural Modifications

Effects of Electron Donating and Electron Withdrawing Groups

Structural modifications may be introduced to EAPs in order to tune in desired properties. The band gap may be engineered by including electron donating groups (EDGs) which decrease the band gap by raising the HOMO. These EDGs include substituents such as those found in 3,4-ethylenedioxythiophene (EDOT) and 3,4-propylenedioxythiophene (ProDOT) (see Figure 4). Inclusion of EDGs also reduces the monomer and polymer oxidation potentials by increasing electron density and increasing resonance stabilization of the resulting charged polymers. A low oxidation potential is

advantageous because it allows for oxidative polymerization, which is typically a highly controllable process. A disadvantage to a low oxidation potential is that it can lead to stability issues.^{2,11}



Figure 4. 3,4-ethylenedioxythiophene (EDOT) (left) and 3,4-propylenedioxythiophene (ProDOT) (right).

Alternatively, electron withdrawing groups (EWGs) can be incorporated to reduce the

band gap by lowering the LUMO. Groups possessing high electron affinity lower the

LUMO and decrease the band gap (Table 1), but they also lower the HOMO which raises

the oxidation potential.² Commonly used electron-withdrawing groups are cyano, nitro,

and carboxy substituents as well as nitrogen-containing heterocycles.

Acceptor	Electron Affinity (eV)
Benzene	-1.12
Pyridine	-0.62
Pyrimidine	0
Pyrazine	+0.25

Table 1. Electron affinities of nitrogen containing heterocycles with benzene shown for comparison^{12,13}

Another method of controlling the band gap is to utilize a donor-acceptor-donor (DAD) approach. This approach is accomplished by alternating electron donating groups such as thiophene moieties and electron accepting groups such as pyrimidine, pyrazine, quinoxaline, benzotriazole, pyridopyrazine, fluorenone and benzothiadizole.¹⁴ By alternating the electron rich donor with the electron poor acceptor, a conjugated polymer is produced that results in a decreased band gap by raising the HOMO energy levels and lowering the LUMO energy levels. The DAD approach also can be used to control the redox and electrochromic behavior of the polymer.²

In addition to controlling optoelectronic properties of EAPs, it may also be desirable to control physical properties. In particular, flexible side chains can be added to impart solubility. Alkoxy side chains lower the band gap by raising the homo while also reducing the oxidation potential.⁷ Alkyl chains may be added to induce solubility, as in poly(3-hexylthiophene), alkylated poly(3,4-ethylenedioxythiophene)s and poly(3,4- propylenedioxythiophene), alkylated poly(phenylenevinylene)s and alkylated poly(1,4-ethylenedioxythiophene)s and alkylated polyfluorenone.^{4,15,16} p-Doping is more commonly seen due to the greater stability of p-doped polymers versus n-doped polymers.⁹

The n-doping process is usually accomplished chemically by using sodium naphthalene or alkali metal vapors. In n-doped systems an electron acceptor substituent can help to stabilize the negative charge along the backbone. If these EWGs are pendant to the polymer they may cause problems by effectively trapping the negative charge. For this reason it may be preferable to incorporate the EWGs in the backbone of the polymer.

Extended Conjugation Monomers

Extended conjugation is an important property to include when designing monomers that will be polymerized to make conducting polymers. This is accomplished by linking aromatic rings together so that the conjugation is spread over many rings. Extending conjugation reduces oxidation potential (by increasing the number of resonance contributors in the radical cation formed during oxidation), making oxidative polymerization easier for the monomer. Another advantage to this strategy is that the polymer properties can be fine-tuned by selecting different functional groups.

Recently, two monomers 1,4-bis[2-(3,4-ethylenedioxythiophene)]-naphthalene (M1) and 2,6-bis[2-(3,4-ethylenedioxythiophene)]-naphthalene (M2) were prepared by Caixia et al. (see Figure 5).¹⁷ These monomers are very similar however they differ as to where the EDOT groups are bonded to the naphthalene. Both the M1 and M2 monomers have extended conjugation, however the M2 monomer has more extended conjugation because the EDOT moieties are bonded to different rings on the naphthalene as opposed to the M1 monomer where the EDOT groups are bonded on the same ring of the naphthalene. When electrochemical polymerization was conducted, it was found that the onset of monomer oxidation was +1.02 V for the M1 monomer and +0.76 V for the M2 monomer, while the band gap for M1 was 3.18 eV and 3.11 eV for M2. These differences between very similar monomers can be ascribed to the greater extended conjugation and planarity of the M2 monomer.¹⁷ The selection of different groups can also significantly affect the properties of the monomer as was shown by Chopin *et al.*¹⁸ In their studies a naphthalene bisimide was substituted with cyano or aryl ethynyl substituents. When the cyano group was directly connected to the naphthyl core, the first

two reduction potentials were significantly decreased due to the ability of the cyano group to be an electron acceptor, and the aryl ethynyl groups red-shifted the absorbance and enhanced the fluorescence quantum yield, making them potential useful dyes.¹⁸



Figure 5. 1,4-bis(2-(3,4-ethylenedioxythiophene))-naphthalene (M1) and 2,6-bis(2-(3,4-ethylenedioxythiophene))-naphthalene (M2)

Various synthetic routes can be employed to achieve extended conjugation monomers. Many of these reactions use transition metal-mediated coupling reactions, in which organometallic species are coupled with aryl halides.² No matter what metal or organometallic species is used, they are all thought to follow the same general mechanism (see Scheme 1). First, the metal undergoes oxidative addition of X-Ar, resulting in loss of two ligand groups. The aryl group from the organometallic species (for example, ProDOT-Bu₂M'X' in Scheme 1 below) is then bonded to the metal atom from the previous transmetallation step, forming a metal halide as a byproduct. Now both aryl groups are bonded to the same metal catalyst atom. Aryl-aryl coupling then ensues via reductive elimination, and the original catalyst is reformed as the two ligand molecules bond to the metal. In the case of dihaloaromatics, the process repeats to yield the di-coupled product.



Scheme 1. General aryl-aryl coupling mechanism for transition metal-mediated coupling

Aryl-aryl couplings are classified by the type of catalyst and organometallic species used; they are often named for the researchers who conducted the fundamental work (see Table 2).² If a palladium (0) compound catalyst is used and the organometallic species is an aryl zinc halide, the reaction is known as a Negishi coupling.¹⁹ A nickel (II) compound catalyst used in conjunction with an aryl magnesium bromide organometallic is known as a Yamamoto coupling or a Grignard coupling.²⁰ A palladium (0) compound used with an aryl trialkyl tin compound is commonly known as a Stille coupling, and if palladium (II) catalyst is used in conjunction with an aryl boronic acid, the reaction is a Suzuki coupling.¹⁹ Finally, the less common combination of a palladium (0) catalyst used with triaryl indium species has been called a Sarandeses coupling reaction.²¹

For instance, Yamamoto couplings work well if either the aryl halide or the aryl magnesium bromide contains electron donating groups, but incorporation of electron donating groups to both the aryl halide and the aryl magnesium bromide prevents the Yamamoto coupling from working.⁷ Switching to Negishi coupling conditions allows the coupling of two electron rich species. Stille coupling reactions are known to tolerate a wide range of functional groups, but they involve the use of highly toxic organotin reagents.¹⁹ The Sarandeses coupling has recently been shown to tolerate nitrogen-containing heterocycles as the aryl halide.²¹

Catalyst	Organometallic Species	Coupling Reaction Name
palladium (0)	aryl zinc halide	Negishi
nickel (II)	aryl magnesium bromide	Yamamoto / Grignard
palladium (0)	aryl trialkyl tin	Stille
palladium (II)	aryl boronic acid	Suzuki
palladium (0)	triaryl indium	Sarandeses

Table 2. Common transition metal-mediated coupling reactions^{19,20,21}

Solubility of EAPs

Processability is key to successful application of EAPs. A great hindrance to processability is insolubility. It has been shown that the addition of long alkyl chains can induce solubility,¹⁵ presumably by reducing interchain interactions. The alkyl chains increase free volume in the polymer and provide nonpolar tails that the solvent can surround. Polythiophene suffers from insolubility, but this issue is resolved by attaching alkyl chains at the 3-position. These modified polythiophenes have shown moderate to high conductivities, and it has also been shown that the longer the alkyl chain the more desirable the electronic properties due to increased planarity induced by the alkyl chains.¹⁵ An unintended consequence of adding alkyl chains is that it can lead to regioirregular polymers (see Figure 6). Regioirregular polyheterocycles are poorly conjugated because the side chain interactions lead to a sterically-driven twist of the backbone.⁴



Figure 6. Regioirregularity is possible in unsymmetrical monomers such as in poly(3-alkylthiophene) (top), but symmetrical monomers like 3,4-(2,2-dibutyl)propylene-dioxythiophene yield only regioregular polymers (bottom).²

Various synthetic methods have been used to prevent regioirregularity, including using symmetrical monomers such as 3,4-[(2,2-dibutyl)propylenedioxythiophene] (see Figure 6) or producing regioregular polymers from unsymmetrical monomers via Grignard metathesis polymerization.^{22,23} The solubility of PPP has also been improved by adding alkyl chains.³ Like polythiophene and PPP, solubility is an issue with PANI. Attempts to improve the solubility of PANI include attaching alkyl, alkoxy, sulfonyl, aryl and amino groups. However, these modifications reduce polymer molecular weight and yields.⁷

With the desire to attach alkyl chains ProDOT is a good choice for several reasons. First, ProDOT has a low oxidation potential (ca. +0.9V vs. Ag/Ag^+) due to the electron rich propylenedioxy substituent.²⁴ Secondly, when polymerizing, the 3- and 4-positions are blocked (see Figure 4); the structure of the molecule forces polymerization to occur at the 2 and 5 positions. Finally, regioirregularity is not a problem with 3,4-(2,2-dialkylpropylenedioxy)thiophene (ProDOT-R₂), because the monomer is symmetrical. In contrast, polymerization of alkylated EDOT would result in a mixture of head to head, head to tail, and tail to tail linkages because the alkyl chain can be on either of the carbons between the oxygen atoms. ProDOT has three carbons between the oxygen; if the second carbon is dialkylated then polymerization will give rise to regioregular polymers and eliminate the possibility of chirality (see Figure 6).

Applications of Electroactive Polymers

Light Emitting Diodes

An exploitable property of EAPs is their ability to display electroluminescence (EL). As electrons are excited from the ground state by an electrical current, the subsequent relaxation results in emission of light.²⁵ In a light emitting diode (LED), also known as a polymeric light emitting diode, PLED the conducting polymer is placed between an anode such as indium tin oxide and a cathode generally made from aluminum, calcium or magnesium.² A voltage is applied and holes are injected from the anode while electrons are injected from the cathode. These charge carriers are then swept through the polymer substrate by a strong electric field.²⁵ In order to produce an intense EL the medium must have a high mobility of charge carriers and the number of injected opposite charge carriers must be balanced.²⁵ There are two major approaches to the design of the polymeric component of PLEDs. The first is to use a single type of donoracceptor polymer so that charge transport and light emission occur within the same monomer. The drawback to this method is that intermolecular charge transfer occurs along the backbone of the polymer resulting in decreased luminescence.²⁵ The second approach is to develop a p-type polymer with n-type electronegative side groups, such as oxadiazole and quinoxaline. The difficulty in this approach lies in the fact that the synthesis of these molecules is complicated.²⁵

Solar Cells

With fossil fuels diminishing, the search for renewable energy sources has received much attention over the last few decades. Organic solar cells offer a promising

solution for a clean renewable energy. Polymer-based components of solar cells can be prepared via deposition of soluble polymer films from solution or via electrochemical polymerization onto large scale printable, flexible films.²⁶ A serious drawback of polymer solar cells, however, is that there is a poor spectral match between the absorption of the polymer (650 nm) and the solar emission (650-700 nm), which effects the efficiency.²⁶ Typically organic solar cells have a p-n heterojunction formed by two polymers one being the donor and the other an acceptor. Some of the donor polymers include PPV derivatives such as poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4phenylenevinylene] (MEH-PPV) and polythiophene derivatives such as poly(3hexylthiophene).²⁶ The acceptor is most commonly the fullerene derivative [6,6]-phenyl C_{61} -butyric acid methyl ester.²⁶

Electrochromics

Electrochromism is the ability to switch color when an electric current is applied. This property has many potential applications, for example an electrochromic polymer could be applied to a window so that it may be switched from clear to "frosted" or opaque or they could be used on eye glasses so that they could go from clear to shaded. Organic electrochromes offer many possibilities due to their ability to switch colors very quickly as they are oxidized or reduced. Organic electrochromes may also be structurally modified to fine tune the desired color.²⁷

Electroactive Polymer-Based Electrochemical Capacitors (EPECs)

Capacitors can deliver energy at very high rates but they generally cannot store large quantities of energy. Current capacitors typically consist of metal oxides like ruthenium oxide. These compounds are problematic because they can cause pollution by leaking into ground water, and they are heavy and expensive. Another drawback of metal oxides is that only the surface of the particles is able to store charge as opposed to EAPs where the entire volume is available to store charge.²⁸ There are many other advantages of polymer-based capacitors including flexible morphologies, chemical stability, high conductivity and lower cost.²⁸ The general make up of an EPEC includes charge collectors, electrolyte, a separator, and two polymer electrodes which may be different polymers or the same.²⁸

Motivation for Research

EAPs have many applications including solar cells, light emitting diodes, batteries, electrochemical capacitors and sensors. Their ability to switch colors between redox states makes them ideal for LEDs and sensors, and they could potentially increase power storage for solar cells and capacitors.

In order to process these polymers they must be soluble and stable, thus the focus of this research. Several soluble DAD monomers were prepared. The impact of the type of acceptor group was studied, as was the effect of modifying electron donating ability of the donor groups of varied electron donating ability. The donor groups consist of ProDOT, EDOT, and thiophene. The acceptor groups include pyrimidine, bipyrimidine, and isopyrazole. Alkyl substituents were incorporated in either the isopyrazole acceptor group or in the ProDOT donor group. The appropriate monomers were synthesized, purified, and characterized. Upon purification, one monomer was polymerized, both chemically and electrochemically. Its band gap was determined in the solid state and in solution and compared to band gaps of other similar polymers.

CHAPTER II

BISDIBUTYLPRODOTPYRIMIDINE

Background

2,5-Bis-(thien-2-yl)-pyrimidine (BTPm) and 2,5-bis-(3,4-ethylenedioxythien-2-yl) pyrimidine (BEPm) were both previously synthesized, polymerized and electoactively characterized in the Irvin group (see Figure 7).^{11,29, 30} Both monomers underwent oxidative polymerization to give insoluble electroactive polymers.²⁹ The ethylenedioxy substituents reduced oxidation potentials of both the monomer and polymer versus the thiophene analouges.²⁹ The band gap of the EDOT-based polymer was found to be 1.8eV; however the thiophene-based polymer's band gap could not be determined because of poor electrochemical stability.²⁹ These differences are due to the dioxy group of EDOT which donates electron density and raises the HOMO.¹⁰



Figure 7. Structures of 2,5-Bis-(thien-2-yl)-pyrimidine (BTPm) (left) and 2,5-bis-(3,4-ethylenedioxythien-2-yl-pyrimidine (BEPm) (right)

Results and Discussion

Synthesis

In an effort to make a more soluble version of BEPm, a new monomer was targeted in which dialkylProDOT rings replace EDOT rings. This monomer, 2,5bis{[3,4-(2,2-dibutylpropyl)propylenedioxy]thien-2-yl}pyrimidine (BProPm-Bu₂) was chosen as a target monomer. EDOT and ProDOT (see Figure 4) have similar oxidation potentials²⁴ but as mentioned earlier, ProDOT is more desirable because it gives regioregular polymers when alkyl groups are attached on the second carbon between the two oxygens of the dioxyalkyl group. Butyl groups were chosen because of the commercial availability of the precursor, 2,2-dibutyl-1,3-propanediol. The 3,4-dibutyl ProDOT (ProDOT-Bu₂) precursor was prepared as per a procedure reported by Welsh *et al.* (see Scheme 2).²² There is no mechanism for transetherification reported in the literature. The first synthesis of this type was reported by Langeveld-Voss *et al.*³¹ A mechanism for transetherification is proposed here (see Scheme 3). It is thought that a $S_{N}2$ reaction occurs twice between the diol and the methoxy groups of 3,4-

dimethoxythiophene resulting in a loss of methanol.



Scheme 2. Synthesis of 3,4-dibutyl ProDOT (ProDOT-Bu₂)



Scheme 3. Proposed mechanism for transetherification of 2,5-bis{[3,4-(2,2-dibutylpropyl)propylenedioxy]thien-2-yl}pyrimidine (ProDOT-Bu₂)

Synthesis of BTPm and BProPm-Bu₂ were first attempted via Negishi coupling (see Scheme 4). The desired compounds were not observed in ¹H NMR spectra of either of the reaction products. It has previously been reported that 2-bromothiophene was successfully coupled to other aromatics via Negishi, so the failure to couple here likely results from an intolerance of Negishi coupling with nitrogen containing species.^{32,33} BProPm-Bu₂ was then successfully synthesized via a Sarandeses reaction; the procedure was adapted from one reported by Mosquera *et al.* (see Scheme 5).²¹



Scheme 4. Negishi coupling of 2,5-Bis-(thien-2-yl)-pyrimidine (BTPm) and 2,5-bis{[3,4-(2,2-dibutylpropyl)propylenedioxy]thien-2-yl}pyrimidine (BProPm-Bu₂) where Ar could be thiophene or ProDOT



Scheme 5. Synthesis of 2,5-bis{[3,4-(2,2-dibutylpropyl)propylenedioxy]thien-2-yl}pyrimidine (BProPm-Bu₂) via Sarandeses coupling

Electrochemistry

Figure 8 shows the electropolymerization of BProPm-Bu₂ using a 0.01 M solution of BProPm-Bu₂ in a 0.1 M solution of 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (EMIBTI) in CH₃CN. On the first cycle, oxidation processes appear at +0.65 V and at +1.05V. The lower oxidation likely involves removal of an electron from the thienyl carbon farthest away from the nitrogens (identified as C_A in Schemes 6 and 7), while the higher oxidation likely results from removal of an electron from the thienyl carbon closest to the nitrogens (identified as C_B in Schemes 6 and 7). C_A oxidizes at lower potentials than C_B , because the resultant radical cation is more stable (has more resonance contributors) than the radical cation from C_B . It can also be seen in Scheme 6 that this route will not result in polymerization. The reduction process centered at -0.75V is likely due to conversion of the radical cation shown in Scheme 6 back to the monomer. Reduction of the polymer (formed from the radical cation shown in Scheme 7) occurs below -1.3V (Figure 9) and therefore is not apparent in Figure 8. As was noted by Winkel *et al.*, cycling to very negative potentials during polymerization is not possible with alkylenedioxythiophene (EDOT or ProDOT, for example) monomers, because of undesirable side reactions of the ether substituent.¹¹ These results are very similar to that of PBEPm reported by Carberry, except that in the PBEPm case, the scan was stopped below the second monomer oxidation process occurred. These processes were not seen with PBTPm. This suggests that the differences are due to the alkylenedioxy group on the PBEPm and PProPm-Bu₂.²⁹


Figure 8. Electropolymerization of 0.01 M BProPm-Bu₂ in 0.1 M EMIBTI / CH₃CN at 100 mV/s for 5 cycles from -1.3 to +1.3 V. WE: Pt (0.2 cm diameter); RE: Ag wire; CE: Pt flag

After electropolymerization, the polymer PBProPm-Bu₂ was rinsed with acetonitrile and placed into monomer free electrolyte solution (0.1 M EMIBTI/CH₃CN). The polymer electrochemisty was studied as a function of scan rate (see Figure 9). The scan rates conducted were 350, 250, 100, 50, and 25 millivolts per second (mV/s). The linear relationship achieved from current response versus scan rate (see Figure 9 inset) indicates that the polymer is electroactive and adhered to the electrode according to the theory of surface immobilized redox centers.³⁴



Figure 9. Cyclic voltammetry of PBProPm-Bu₂ grown in 0.1M EMIBTI/CH₃CN at 100mV/s and cycled in 0.1M EMIBTI/CH₃CN at 25, 50, 100, 250, and 350 mV/s from - 1.8 to +1.3V. WE: Pt (0.2cm diameter); RE: Ag wire; CE: Pt flag. Inset: The linear relationship between peak current and scan rate reveals that the polymer film is electroactive and adhered to the electrode.



Scheme 6. Resonance contributors for the oxidation of 2,5-bis{[3,4-(2,2-dibuty]propy])propylenedioxy]thien-2-yl}pyrimidine (BProPm-Bu₂) that results from a removal of an electron from C_B ; this process is unfavorable due to the limited number of resonance contributors. Note also that none of the resonance contributors can react further to form dimer, so reduction back to the monomer can occur.



Scheme 7. Resonance contributors for the oxidation of 2,5-bis{[3,4-(2,2-dibutylpropyl)propylenedioxy]thien-2-yl}pyrimidine (BProPm-Bu₂) that results from removal of an electron from C_A . Here, coupling can occur at the radical site shown in the final resonance contributor, ultimately leading to polymerization.

Band Gap Determination

The band gap was determined both in the solid and liquid state. BProPm-Bu₂ was chemically polymerized by adding ferric (III) chloride (7.77 x 10^{-5} mol, 0.0290 g) to a solution of BProPm-Bu₂ (7.77 x 10^{-5} mol, 0.0476 g) in 2 mL of deuterated chloroform.

After addition of the oxidant, the red solution was stirred overnight. After 24 hours had passed, one drop of hydrazine was added to neutralize the PBProPm-Bu₂. An aliquot was taken from the neutralized polymer solution and dropped onto two separate indium tin oxide coated glass slides. The slides were dried under vacuum overnight to remove solvent. One of the slides was then placed in an aqueous solution of ferric (III) chloride (to yield oxidized polymer), and the other slide was placed in a solution of chloroform and hydrazine (to ensure neutralized polymer). A UV-Vis spectrum was then taken for both the oxidized and neutralized polymer films (see Figure 10). The bandgap was determined to be 1.6 eV.



Figure 10. UV-Vis absorption of the neutral and p-doped films of PBProPm-Bu₂

To determine the absorption and bandgap of the polymer in solution, an aliquot of the neutralized polymer in CDCl₃ was diluted tenfold (twice). A drop of hydrazine was added to ensure the polymer was neutralized, and a spectrum was obtained (see Figure 11). The original solution was pale brown and after addition of hydrazine it became a bright yellow. A few crystals of iodine were then added to the original solution of polymer and $CDCl_3$ and it was left to stir overnight, the brown solution became a fuchsia red color. An aliquot of this solution was then diluted tenfold (twice), and a UV-Vis spectrum was obtained (see Figure 11).



Figure 11. UV-Vis absorption of the neutral and oxidized solution of PBProPm-Bu₂ in $CDCl_3$

The bandgap in solution was determined to be 2.3 eV. This value is much higher than what was determined for the solid state (1.6eV). In the solid state, the polymer is much more immobilized than it is in solution. This allows for pi stacking between adjacent polymer chains and thus the band gap is decreased due to more easily accessible discrete new levels in the band gap; this type of behavior has been previously witnessed as noted by Irvin.³⁵

Experimental

Materials

3,4-Dimethoxythiophene was purchased from Aldrich Chemical. *p*-Toluenesulfonic acid, 4Å molecular sieves (activated by drying in an oven 24h at 100°C), 2,2-dibutyl-1,3-propanediol, 2-bromothiophene, 0.5 M zinc chloride solution in hexanes, 2.5 M butyllithium in hexanes, anhydrous tetrahydrofuran (THF), ferrocene and deuterated NMR solvents were purchased from Acros Chemical. Magnesium sulfate, hydrochloric acid, sodium hydroxide, ethyl acetate, hexane, dichloromethane and toluene were purchased from Fisher Scientific. Indium (III) chloride was purchased from Alfa Aesar and stored in an inert atmosphere glove box. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and 5-bromo-2-chloropyrimidine (BCPm) were purchased from Frontier Scientific. Acetonitrile (CH₃CN, anhydrous) was purchased from Sigma-Aldrich. Cellulose extraction thimbles were purchased from Whatman. Silica gel 75-250 microns was purchased from Mallinckrodt Silicar. NMR tubes were purchased from Wilmar. All materials and chemicals were used as received unless otherwise noted.

Characterization

Structural Identification

Structural identification accomplished using ¹H and ¹³C NMR. Spectra were obtained with a Bruker Avance III 400 MHz NMR.

Electrochemistry

Electropolymerization of BProPm-Bu₂ was accomplished using a 0.01 M BProPm-Bu₂ monomer dissolved in a 0.1 M EMIBTI/CH₃CN solution. Cyclic voltammetry experiments were conducted using a Pine WaveNow potentiostat in an anhydrous argon atmosphere glovebox. The working electrode, pseudo-reference and auxiliary electrodes were a platinum button (0.2 cm diameter, Bioanalytical Systems Inc.), a silver wire, and a platinum flag, respectively. All cyclic voltammograms were referenced to the ferrocene/ferrocenium couple in the electrolyte.³⁶

UV-Vis

UV-Vis spectra were accomplished using a BioTek Synergy H4 Hybrid Reader. ITO glass slides were purchased from Delta Technologies, 8-10Ω resistance.

Synthesis

3,3-Dibutyl-3,4-dihydro-2H-thieno[3,4-b]-[1,4] dioxepine (ProDOT-Bu₂)

As reported by Welsh,²² 3,4-dimethoxythiophene (0.0139 mol, 2.00 g), 2,2 dibuyl-1,3-propanediol (0.0277 mol, 5.22 g) and *para*-toluene sulfonic acid (PTSA) (0.00387 mol, 0.74 g) were added to 150 mL toluene in a single neck flask with a soxhlet extractor filled with 4Å molecular sieves to remove methanol. The reaction was refluxed for one day at 110 °C then washed with deionized water. The organic layer was dried over MgSO₄, filtered with vacuum through paper and purified with a silica column using a 3:2 hexane/methylene chloride mixture as the elutant. The product was the first to elute and had an R_f value of 0.67. Solvent was removed using a rotary evaporator to yield a clear viscous liquid (75% yield). ¹H NMR (CD₂Cl₂) δ 6.41 (s, 2 H), 3.83 (s, 4H), 1.19-1.43 (m, 12 H), .92 (t, 6 H). Lit:³⁷ ¹H NMR (CDCl₃, 300 MHz) δ 6.42 (s, 2H), 3.85 (s, 4H), 1.20-1.42 (m, 12H), 0.92 (t, 6H)

Attempted Synthesis of 2,5-Bis-(thien-2-yl)-pyrimidine (BTPm) via Negishi Coupling

Following a procedure adapted from J. Irvin,⁷ 2-bromothiophene (0.0184 mol, 3.0 g) was added to a flame dried reaction flask purged with argon along with 15 mL of anhydrous THF. The reaction flask was chilled to -78°C and n-butyllithium (0.018 mol, 7.3 mL) was added dropwise. The mixture was allowed to stir for one hour at -78°C. In another flame dried reaction flask purged with argon, zinc chloride a 0.5 M solution in hexanes (0.019 mol, 38 mL) was added along with 15 mL of anhydrous THF and chilled to 0°C. The lithiated thiophene was then transferred via cannula dropwise into the solution of zinc chloride. This mixture was allowed to stir for one hour at 0°C. A flame dried reaction flask was then charged with 10 mL anhydrous THF, 2-chloro-5bromopyrimidine (BCPm) (0.004593 mol, 0.8884 g) and tetrakis(triphenylphosphine)palladium(0) $(2.379 \times 10^{-5} \text{ mol}, 0.0275 \text{ g})$. The thiophene zinc chloride solution was then added to the flask containing the BCPm, and the mixture was stirred at 50°C for five days under argon. The solvent was then removed under reduced pressure and the crude product was dissolved in dichloromethane. The organic layer was washed sequentially with 5% hydrochloric acid, water and 1 M sodium hydroxide. A proton NMR was then performed on the crude product, purification was not deemed necessary because the intended product was not found.

Attempted Synthesis of BProPm-Bu₂ via Negishi

The procedure described above for the attempted synthesis of BTPm via Negishi coupling was followed using ProDOT-Bu₂ (0.007896 mol, 2.1195 g), n-butyllithium (0.0079 mol, 3.2 mL), 0.5 M zinc chloride (0.008267 mol, 16.5 mL) 5-bromo-2-chloropyrimidine (0.001971 mol, 0.3813 g), and tetrakis(triphenylphosphine)-palladium(0) (1.0209 x 10^{-5} mol, 0.0118 g). The proton NMR showed large amounts of starting material made and little to no product formed.

BProPm-Bu₂ via Sarandeses

Synthesis was adapted from Mosquera *et al.* (Figure 8).²¹ All reaction mixtures were kept under argon. ProDOT-Bu₂ (0.00745 mol, 2.00 g) was combined with 13 mL of dry THF in a flame dried 3-neck flask under argon. The mixture was chilled to -78 °C using a dry ice/acetone bath. n-Butyl lithium (0.0082 mol, 3.3 ml) was added dropwise and then the reaction was stirred for one hour at -78 °C. In a dry argon atmospher, indium (III) chloride (0.00273 mol, 0.604 g) was placed in a 3-neck flask along with 54 mL dry THF to make a 0.05 M solution. The mixture was then removed from the glovebox and cannula transferred into the lithiated ProDOT-Bu₂ mixture. The combined mixtures were stirred for an hour at -78 °C and then for an additional hour at room temperature. Another flame dried 3-neck flask was charged with 2-chloro-5-bromo pyrimidine (BCPm) (0.00248 mol, 0.48 g), Pd(PPh₃)₄ (6.24 x 10⁻⁵ mol, 0.072 g) and 4 mL of dry THF via syringe. The In(ProDOT-Bu₂)₃ solution was transferred via cannula to the BCPm solution. The reaction was allowed to run for 3 days. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane. The reaction was then washed sequentially with 5% HCl, saturated ammonium chloride and brine. The crude product was a dark orange viscous oil. Four silica gel columns were performed in order to purify the crude product. The first column used had a 5:95 ethyl acetate/hexane mixture, the unreacted ProDOT-Bu₂ had an R_f value of 0.84 and was the first to elute. Four fluorescent spots followed, and the product was contained in a blue fluorescent spot located at an R_f of 0.53. A ¹H NMR performed on this fraction showed that it still contained impurities due to insufficient separation. This was further purified using a second column with a 2:3 hexane/dichloromethane mixture. The product eluted with an R_f value of 0.58 and the proton NMR showed that it contained mono and disubstituted product. Thin layer chromatography (TLC) of this fraction (elutant: 2:3 hexane/dichloromethane) revealed four very close blue fluorescent spots. The third column performed was a 10:90 ethyl acetate/hexane mixture. The product again eluted with impurities having an R_f of 0.56; this fraction was further purified with a fourth column. The fourth column used was a 5:95 ethyl acetate/hexane mixture; this time a pure sample was obtained. Upon solvent removal under reduced pressure, the purified BProPm-Bu₂ was a light vellow, fluorescent (blue) oil with a melting point below 25 °C. The amount obtained was 0.3756 g, a 24.7 % yield. It is assumed that a fair amount of product was lost in the purification process. ¹H NMR (CD₂Cl₂) δ 8.95 (s, 2H), 6.55 (s, 1H), 6.48 (s, 1H), 4.02 (s, 2H), 3.97 (s, 2H), 3.90 (s, 4H), 1.51 (m, 24H) .91 (tt, 12H). ¹³C NMR (CDCl₃, 400 MHz) δ 153.51, 150.57, 150.30, 147.73, 124.31, 120.08, 114.02, 108.97, 104.25, 78.33, 77.54, 77.49, 77.43, 77.22, 53.41, 43.76, 43.70, 31.83, 31.71, 25.05, 25.03, 23.50, 14.03, 14.01.

CHAPTER III

BISTHIENYLBIPYRIMIDINE

Background

Several attempts had previously been made by the Irvin group to synthesize bisthienyl bipyrimidine (Figure 12).³⁰ It was theorized that having two acceptor groups in the monomer would increase the electron affinity of molecule and thus decrease the reduction potential. This would hypothetically lead to a better n-doped polymer.



Figure 12. Bis-thienyl bipyrimidine (BTBPm) structure

Katie Winkel, a previous student in the Irvin lab, tried several synthetic routes. A Suzuki reaction was first used to couple 5-bromopyrimidine with 2-boronic acid thiophene (see Scheme 8). The product 5-thien-2-yl pyrimidine was purified and an attempt was made to brominate at the 2-position of pyrimidine (see Scheme 8).³⁰ This was unsuccessful, and instead the monomer was brominated at the 2 and 5-position of the thiophene.³⁰ It was then determined that the synthesis should proceed from the inside out.



Scheme 8. Synthesis of 3-(thien-2-yl)-pyrimidine via Suzuki and bromination

Winkel also attempted an Ullmann coupling using 5-bromo-2-chloropyrimidine to produce 5,5'-dibromo-2,2'-bipyrimidine (see Scheme 9).³⁰ Unfortunately the crude product was too complex to achieve separation.³⁰



Scheme 9. Synthesis of 5,5'-dibromo-2,2'-bipyrimidine via Ullmann

Another attempt made by Winkel was a second inside-out approach by coupling two 2-chloropyrimidine monomers to synthesize bipyrimidine followed by bromination at the 5 position of the pyrimidine, but once again separation was not achieved due to the singly and doubly brominated bipyrimidine (see Scheme 10).³⁰



Scheme 10. Synthesis of 5,5'-dibromo-2,2'-bipyrimidine using and inside-out approach

Results and Discussion

Synthesis

A Sarandeses reaction was successful in synthesizing the precursor 2-chloro-5-(thien-2-yl)pyrimidine (ThClPm) (see Scheme 11).²¹ The product was purified by recrystallization from cyclohexane. This precursor was then used in a second Sarandeses reaction to couple ThClPm to itself (Scheme 12). Although the proton NMR of the crude product revealed that there may be some small amount of product in the mixture, it was also noted that there were multiple peaks in the 8.6 to 8.9 ppm region indicating that multiple species had been formed, most likely due to lithiation of the thiophenes leading to coupling at the 5-position of the thiophene in the ThClPm monomer and the 2-postion of the pyrimidine in a second ThClPm monomer (see Scheme 13). Lithiation may not have been successfully accomplished due to the melting point of the solvent used (1,2dimethoxyethane (glyme)). The glyme froze at -78 °C so lithiation was carried out at 0 °C instead. The glyme was initially chosen as a solvent because its boiling point is higher than THF. It was theorized that running the reaction at a higher temperature would improve the synthesis. Another indicator that the reaction was unsuccessful was that the proton NMR showed a large amount of the ThClPm starting material remaining.



Scheme 11. Synthesis of 2-chloro-5-(thien-2-yl)pyrimidine (ThClPm)



Scheme 12. Attempted synthesis of bis-thienyl bipyrimidine (BTBPm) where the X is either I or Cl



Scheme 13. Possible competing reaction in attempted synthesis of BTBPm

A second attempt was made using the precursor 2-iodo-5-(thien-2-yl)pyrimidine (ThIPm) (see Scheme 14) in order to investigate whether the change in halogen would make the synthesis more successful. In general iodoaryl compounds have a much higher reactivity in cross coupling reactions because iodide is a better leaving group than either bromide or chloride.³⁸ The procedure used to synthesize the ThIPm was adapted from Vlad *et al.*³⁸ The Sarandeses reaction was used to synthesize the BTBPm once the precursor had been made. (Scheme 12). The proton NMR of the crude product looked very similar to that of the synthesis previously mentioned using ThClPm. Once again multiple peaks where seen in the 8.6 to 9.2 ppm region most likely due a non-selective lithiation step to form the BTBPm. There was also a large amount of starting material remaining. Purification was not attempted, and the BTBPm monomer was not successfully synthesized.



Scheme 14. Synthesis of 2-iodo-5-(thien-2-yl)pyrimidine (ThIPm)

Experimental

Materials

2-Bromothiophene, n-butyllithium (2.5M in hexanes), and anhydrous THF were purchased from Acros. Pd(PPh₃)₄ and BCPm were purchased from Frontier Scientific. Indium (III) chloride was purchased from Alfa Aesar and stored in an inert atmosphere glove box. Hydrochloric acid, ammonium chloride, diethylether, cyclohexane, dichloromethane, 57% hydroiodic acid, 1,2-dimethoxyethane (glyme), methanol, and magnesium sulfate were purchased from Fisher Scientific. All chemicals were used as received.

Structural Identification

Structural identification was accomplished via ¹H NMR. Spectra were obtained using Bruker Avance III 400 MHz NMR.

Synthesis

2-Chloro-5-(thien-2-yl)-pyrimidine (ThClPm)

The synthesis was adapted from Mosquera et al.²¹ All reaction mixtures where kept under argon. A flame dried reaction flask was charged with 50 mL of dry THF via cannula. 2-Bromothiophene (0.03099 mol, 3 mL) was then added dropwise via syringe. The reaction flask and mixture were chilled to -78 °C in a dry ice acetone bath. Once the mixture was brought to temperature n-butyl lithium (0.0341 mol, 13.4 mL) was added dropwise via syringe. The reaction was then stirred at -78 °C for one hour. A separate flame dried reaction flask was brought into the glovebox where it was then charged with 227 mL dry THF and indium (III) chloride (0.01136 mol, 2.5 g) to make a 0.05 M solution. This solution was then slowly added via cannula to the lithiated thiophene mixture while maintaining the temperature at -78 °C, and the mixture was stirred for one hour. The reaction mixture was then allowed to return to room temperature and stir for an additional hour. A flame dried flask was purged with argon and then charged with 60 mL of dry THF via cannula. 2-Chloro-5-bromo pyrimidine (0.0304 mol, 5.88 g) and tetrakis(triphenylphosphine)palladium(0) $(1.3848 \times 10^{-4} \text{ mol}, 0.16 \text{ g})$ were then added to the flask containing the 60 mL of THF. The tri thienyl indium mixture was then slowly transferred via cannula to the reaction flask containing the BCPm and palladium catalyst. The reaction mixture was heated at reflux and stirred under argon for two and a half days. The crude mixture was a dark orange color. The solvent was removed under reduced pressure, and then diethyl ether was used to dissolve the residue. The dissolved crude product was then transferred to a separatory funnel, and where it was washed sequentially with 1M hydrochloric acid, saturated ammonium chloride and brine (three times each). The organic layer was then dried over magnesium sulfate and filtered through paper. The solution was then concentrated under reduced pressure to yield a bright yellow solid that fluoresced under UV light. The solid was purified via recrystallization from cyclohexane to produce 1.8487 g (31%) ThCIPm. Mp: 120-122 °C. (Lit:²¹ 122-125 °C). ¹H NMR (CDCl₃,400 MHz) δ 8.81 (s, 2H), 7.46 (br d, 1H), 7.40 (br d, 1H), 7.17 (dd, 1H). Lit:^{21 1}H NMR (CDCl₃, 300 MHz) δ 8.82 (s, 2H), 7.47 (br d, 1H), 7.41 (br d, 1H), 7.18 (dd, 1H).

2-Iodo-5-(thien-2-yl)pyrimidine (ThIPm)

The procedure was adapted from Vlad *et al.*³⁸ In a flame dried reaction flask under argon ThClPm (0.4728 g, 2.404 x 10^{-3} mol) was dissolved in 20 mL of dichloromethane and chilled to 0°C. In a separate flask hydroiodic acid (HI, 57%) (8 x 10^{-3} mol, 1.1 mL) was chilled to 0°C and then added dropwise to the dissolved ThClPm and stirred at 0°C. Upon addition of HI the mixture turned red and then orange. The reaction was monitored via proton NMR. After 24 hours the reaction was not complete as noted by remaining starting material, so additional HI (2 mL) was added and the reaction was allowed to stir for 48 hours at room temperature. Potassium carbonate was then added to the reaction mixture until the formation of gas subsided. At this point the crude mixture was dark red. The mixture was decolorized with a saturated solution of sodium thiosulfate, which caused the color to change from dark red to yellow. This mixture was then poured into a separatory funnel and extracted with dichloromethane. The organic layer was dried with sodium carbonate and filtered through paper, and the solvent was removed under reduced pressure. The yellow solid was recrystallized from cyclohexane to leave 0.9915 g (47%) ThIPm. ¹H NMR (CDCl₃,400 MHz) δ 8.81 (s, 2H), 7.46 (br d, 1H), 7.40 (br d, 1H), 7.17 (dd, 1H).

5,5'-Bis-(thien-2-yl)-2,2'-bipyrimidine (BTBPm)

The procedure was adapted from *Mosquera et al.*²¹ The same procedure was used for the ThIPm starting material. ThClPm $(3.1 \times 10^{-3} \text{ mol}, 0.60 \text{ g})$ was added to a flame dried reaction flask under argon and was then charged with 10 mL of glyme and chilled to 0°C. n-Butyllithium (3. 3 x 10^{-3} mol, 1.3 mL) was then added dropwise and stirred for one hour at 0°C. A schlenk flask was brought into an inert argon atmosphere and indium (III) chloride $(3.1 \times 10^{-3} \text{ mol}, 0.70 \text{ g})$ was added along with 60 mL of dry glyme. This solution was removed from the glove box and slowly cannula transferred to the solution of lithiated ThClPm. This solution was stirred for one hour at 0°C then allowed to warm to room temperature and stirred for an additional hour. ThClPm $(3.1 \times 10^{-3} \text{ mol. } 0.60 \text{ g})$ was added to a flame dried reaction flask under argon. It was then charged with 10 mL of glyme and tetrakis(triphenylphosphine)palladium(0) $(9.2 \times 10^{-5} \text{ mol}, 0.11 \text{ g})$. The triorgano indium mixture was then transferred to the reaction flask containing the ThClPm, glyme and catalyst. It was left to stir for 72 hours at reflux. The reaction mixture was then allowed to cool to room temperature and quenched with 3 mL of methanol. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane. The organic phase was then washed sequentially with 5% hydrochloric acid, saturated ammonium chloride, and brine (three times each). The organic layer was then dried over magnesium sulfate and filtered through paper. The dichloromethane was removed under reduced pressure. The proton NMR showed an excessive amount of

starting material remaining and multiple products. The reaction was deemed unsuccessful and no further purification was performed.

CHAPTER IV

BISTHIENYLHEXADECYLISOPYRAZOLES

Background

Previously Witker et al. reported a novel DAD polymer based on 3,5-bis(thien-2yl)-4.4-dimethylisopyrazole (BTIPz) (see Figure 13).³⁹ This monomer was promising because during electropolymerization relatively stable n-doping and p-doping processes were observed and degradation was not significant.³⁹ Unfortunately, the electron withdrawing ability of the isopyrazole group in combination with relatively difficult-tooxidize thiophene donor groups caused the monomer to have a high oxidation potential which made electropolymerization difficult and required long cycling times to produce a film adequate for electrochemical analysis.³⁹ In order to remedy this problem Winkel synthesized 3,5-bis-(3,4-ethylenedioxythien-2-yl)-4,4-dimethyl isopyrazole (BEIPz) (Figure 13).³⁰ The thiophene groups were replaced by EDOT in order to lower the oxidation potential. It was found that cycling to n-doping potentials during polymerization was unsuccessful due to irreversible reduction processes.¹¹ However, oxidative polymerization produced a polymer with lower oxidation potential than the analogous thiophene monomer, and the novel polymer (PBEIPz) exhibited readily accessible p-doping and n-doping processes.²⁹

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Figure 13. Structures of 3,5-bis(thien-2-yl)-4,4-dimethylisopyrazole (BTIPz) (left) and 3,5-bis-(3,4-ethylenedioxythiophen-2-yl)-4,4-dimethyl isopyrazole (BEIPz) (right)

To build upon this previous work in an attempt to produce a soluble n-doping polymer, the syntheses of BTIPz and BEIPz containing long alkyl chains (Figure 14) were attempted. It was hoped that the incorporation of hexyl or hexadecyl side chains would induce solubility while maintaining the excellent p- and n-doping processes of PBEIPz.



Figure 14. Structures of BTIPz-R₂ (left) and BEIPz-R₂ (right) where $R = C_6H_{13}$ or $C_{16}H_{33}$

Results and Discussion

In order to synthesize the starting material first the two acidic hydrogens on diethyl malonate were removed with a strong base and replaced by two hexyl or hexadecyl chains by adding 1-bromohexane or 1-bromohexadecane (see Scheme 15). When the procedure was attempted in a stepwise fashion, (e.g. one equivalent of NaH, one equivalent of $BrC_{16}H_{33}$, a second equivalent of NaH, and finally a second equivalent of $BrC_{16}H_{33}$) the diethylmalonate was successfully dialkylated.



Scheme 15. Synthesis of 2,2-dihexyl-1,3-diethyl ester (DEM-H₂) and 2,2-dihexadecyl-1,3-diethyl ester (DEM-HD₂) where $R = C_6H_{13}$ or $C_{16}H_{33}$

Attempts were then made to saponify both esters using potassium hydroxide. The reaction was acidified to ensure conversion to the diacid. Unfortunately only the hexadecyl-containing diacid could be collected. It was interesting to note that in the work up of the dihexadecyl diacid, the product was found in the aqueous layer and only a very small amount of product was found in the organic layer. The product contained in the organic layer was un-saponified starting material. This was contrary to the procedure followed which maintained that the product could be extracted with ether.⁴⁰ It would seem that having two hexadecyl chains would cause the product to reside in the organic

layer, but the hydrogen bonding of the diacid groups must have exceeded the strength of the intermolecular bonds between the hexadecyl chains and the organic solvent.

A new workup procedure was then outlined where in the aqueous layer was acidified to ensure conversion to the acid and the water was removed under reduced pressure. The resulting white solid contained potassium chloride and the product. Ethanol was then added to this solid causing the product to dissolve while almost all the KCl remained undissolved. Though this molecule has been previously synthesized, a melting point has not been reported.⁴⁰ Removal of the salt was also confirmed by the fact that all the solid had melted at this temperature; if salt had remained it would not have melted these temperatures.



Scheme 16. Synthesi of 2,2-dihexadecylpropanedioic acid (DiAcid-HD₂)

The dialkylated di-acid was then successfully converted to the diacid chloride (see Scheme 17), and no purification was required. This dichloride was a novel compound and was characterized using proton and carbon NMR.



Scheme 17. Synthesis of 2,2-dihexadecyl-1,3-malonyldichloride (MalCl-HD₂)

A nucleophilic acyl substitution was then performed on the dichloride to attach the thiophene or EDOT groups (see Scheme 18). The ring was then closed to form the isopyrazole ring with hydrazine.



Scheme 18. Synthesis of 4,4-dihexadecyl-3,5-bis(thien-2-yl)isopyrazole (BTIPz-HD₂)

In the synthesis of BTIPz set forth by Witker *et al.*, a Negishi coupling was employed in a two-step synthesis.³⁹ It was noted however in the work done by Winkel that a nucleophilic acyl substitution without the use of a catalyst was successful in synthesizing BEIPz thus eliminating the need for expensive catalysts.³⁰ A one-pot synthesis was conducted to synthesize BTIPz-HD₂ and BEPIz-HD₂ after it was found that attempting to purify the intermediate was not successful and led to loss of product. Ring closure was successful, but a deviation from the literature was required. It was found that when a 10 to 1 molar excess of hydrazine to precursor was used the ring closure was incomplete as seen by NMR. However, when this amount was changed to a 1.1 to 1 molar excess, the ring was closed. This was noted by a disappearance of a proton NMR peak in the 8 ppm region. Three columns were used to purify $BTIPz-HD_2$ due to many side products. The choice of column was changed from silica to alumina after staining of the silica column was seen. This was likely due to a reaction between the acidic silica and the lone pairs of the nitrogens on the isopyrazole ring. When the stationary phase was switched to neutral alumina, this problem was not encountered. Purification was limited by the fact that the product was an oil; recrystallization and sublimation were not an option. Using thin layer chromatography (TLC), many solvent mixtures were tested to improve separation of the product and by-products; only minimal separation was achieved. The multitude of side reactions was exasperated by the one-pot synthesis. It is theorized that if purification could have been achieved with the intermediate, the final product may have been possible to purify. $BTIPz-HD_2$ was not successfully purified, and BEIPz-HD₂ awaits attempts at purification.

No mechanism for the ring closure has been found in the literature, but one is postulated here (see Scheme 19). In the first step there is nucleophilic attack on one of the carbonyl carbons by a nitrogen of a hydrazine molecule. A proton transfer then occurs between the attacking nitrogen and the carbonyl oxygen bonded to the attacked carbon. The free nitrogen on the same hydrazine molecule then attacks the second carbonyl carbon and another proton transfer occurs between the attacking nitrogen and carbonyl oxygen. It is assumed that when there is a large excess of hydrazine to intermediate, the second nitrogen attack on the second carbonyl carbon occurs with a second hydrazine molecule. When there is limited hydrazine, the likelihood of the same hydrazine molecule attacking twice is greatly increased. The newly formed alcohols then accept the remaining protons on either nitrogen, and the ring is closed evolving water as a byproduct.



Scheme 19. Proposed mechanism of isopyrazole ring closure

Experimental

Materials

Diethyl malonate and sodium hydride (57-63% oil dispersion) were purchased from Alfa Aesar. Anhydrous THF, 1-bromohexadecane, 2-bromothiophene, nbutyllithium and neutral alumina (50-200 micron) were purchased from Acros. Potassium hydroxide, ethanol, ethyl acetate and hexanes were purchased from Fisher Scientific. Hydrazine was purchased from Sigma Aldrich. Thionyl chloride was purchased from Tokyo Chemical Industry. All materials and chemicals were used as received.

Structural Identification

Structural identification accomplished via ¹H and ¹³C NMR. Spectra were obtained using Bruker Avance III 400 MHz NMR.

Synthesis

2,2-Dihexadecyl-1,3-diethyl ester (DEM-HD₂)

The procedure was adapted from *Deline et al.* (see Scheme 13).⁴⁰ A flame dried flask under argon was charged with 500 mL of anhydrous THF. Sodium hydride (6.243 x 10^{-2} mol, 1.50 g) was then added to the flask under positive argon. Diethyl malonate (6.2 x 10^{-2} mol, 9.5 mL) was then slowly added to the flask via syringe. Once the mixture went from white to clear, 1-bromohexadecane (6.243 x 10^{-2} mol, 10.3 g) was added. The reaction was left to reflux for 20 hours, then allowed to cool to room temperature. The second addition of sodium hydride (9.364 x 10^{-2} mol, 2.25 g) was slowly dropped into the

reaction and allowed to stir 4 hours at room temperature. 1-Bromohexadecane (9.364 x 10^{-2} mol, 15.46 g) was then added, and the reaction was left to reflux an additional 20 hours. The reaction was cooled to room temperature, and the sodium bromide was filtered through paper. The solvent was removed under reduced pressure to leave a yellow oil. The crude product was purified via simple distillation. The product began to distill at 203 °C to give a clear viscous oil weighing (5.46 g, 27%). ¹H NMR (CDCl₃,400 MHz) δ 4.17 (q, 2H), 1.24 (t, 3H), 1.6 to 1.1 (br m, 60H), 0.88 (t, 6H).

2,2-Dihexyl-1,3-diethyl ester (DEM-H₂)

The procedure outlined above for DEM-HD2 was followed, using the same amounts of starting material. The only difference was that 1-bromohexane was used instead of 1-bromohexadecane. The resultant clear viscous oil was obtained in 85 % yield. ¹H NMR (CDCl₃,400 MHz) δ 4.26 (q, 2H), 1.24 (t, 3H), 1.6 to 1.1 (br m, 60H), 0.88 (t, 6H).

2,2-Dihexadecylpropanedioic acid (DiAcid-HD₂)

The procedure was adapted from Deline *et al.* (see Scheme 14).⁴⁰ DEM-HD₂ $(4.21 \times 10^{-2} \text{ mol}, 25.64 \text{g})$, potassium hydroxide (0.421 mol, 23.6 g), deionized water (150 mL), and ethanol (150 mL) were combined in a reaction flask. The reaction mixture was refluxed overnight. The solvent was then removed under reduced pressure to leave a white solid. The solid was then added to ethanol, and the potassium chloride byproduct was filtered out with paper. The ethanol filtrate containing the product was then heated under vacuum to remove half of the ethanol and then cooled to 0°C. The product was crystallized as a white solid (24.54 g, 33%). Mp 265-270 0°C.

2,2-Dihexadecyl-1,3-malonyldichloride (MalCl-HD₂)

In a procedure adapted from Deline *et al.* (see Scheme 15).⁴⁰ DiAcid-HD₂ (0.014 mol, 8.19g) was combined with thionyl chloride (0.2742 mol, 20 mL) in a flame dried round bottom flask under argon. The solution was stirred at 60°C for 16 hours. The excess thionyl chloride was then removed under reduced pressure. The brown viscous oil (6.71 g, 79%) required no further purification. ¹H NMR (CDCl₃,400 MHz) δ 4.17 (q, 2H), 1.24 (t, 3H), 1.6 to 1.1 (br m, 60H), 0.88 (t, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ 172.04, 171.07, 169.37, 67.93, 61.93, 60.88, 57.56, 32.13, 32.03, 31.93, 29.84, 29.70, 29.67, 29.66, 29.62, 29.58, 29.54, 29.47, 29.41, 29.36, 29.21, 29.09, 23.89, 23.66, 23.54, 22.69.

4,4-Dihexadecyl-3,5-bis(thien-2-yl)isopyrazole (BTIPz-HD₂)

Using a procedure adapted from Witker *et al.* (Scheme 16).³⁹ 2-Bromothiophene (0.021 mol, 2.0 mL) was placed in a flame dried reaction flask under argon and charged with 15 mL of anhydrous THF. The mixture was chilled to -78 °C and n-butyllithium (0.021 mol, 8.5 mL) was added drop wise. In a separate flame dried flask under argon MalCl-HD₂ (8.477 x 10^{-3} mol, 5.0g) was added and charged with 30 mL of anhydrous THF. The MalCl-HD₂ solution was then added dropwise via cannula to the lithiated thiophene. The reaction was then refluxed for three days. The solvent was then removed under reduced pressure, and 50 mL of toluene was added under argon. Hydrazine (0.3 mol, 0.3 mL) was added and the reaction was left to reflux for 96 hours. In an effort to purify the crude dark orange oil, an aluminum oxide column with a 30/70 ethyl acetate / hexane mixture was used. The first fraction eluting contained the product, but it still

contained impurities. The oil was then passed through a short plug of aluminum oxide using hexanes as the elutant. The product did not elute, though some impurities did. The product was then removed from the short plug using ethyl acetate. A second column was used to further purify, the column used was aluminum oxide and a 5/95 ethyl acetate / hexane mixture. Purification remained elusive, though many contaminants were removed. ¹H NMR (CDCl₃,400 MHz) δ 7.69 (m, 1H), 7.51 (m, 1H), 6.92 (m, 1H), 1.9 to 1.0 (br m, 60H), 0.87 (t, 6H).

3,5-Bis-(3,4-ethylenedioxythien-2-yl)-4,4-dihexadecyl isopyrazole (BEIPz-HD₂)

The same procedure was used to prepare BEIPz-HD₂ as was used to prepare BTIPz-HD₂. MalCl-HD₂ (8.477 x 10^{-3} mol, 5.0 g), n-Butyllithium (0.021 mol, 9.3 mL), TMS-EDOT (0.02119 mol, 4.54 g) were the amounts used. The monomer has been synthesized and awaits purification via column chromatography. If purification is achieved, the TMS groups will be removed and the electrochemistry of the monomer will be studied.

CHAPTER V

CONCLUDING REMARKS

Synthesis

In synthesizing the BTPm and BProPm-Bu₂ it was shown that the Negishi coupling reaction could not be used with halopyrimidines. The Sarandeses reaction was successful in producing BProPm-Bu₂. Chemical oxidative polymerization using ferric (III) chloride yielded a polymer that was soluble in acetone and chloroform. As the reaction proceeded, the oxidized polymer was red while the neutral polymer was green. Electrochemical polymerization revealed that there were two separate onsets of monomer oxidation. Resonance structures were drawn to show that BProPm-Bu₂ can only successfully polymerize by one route. The band gap was determined both in the solid and the solution phase to give 1.6 eV and 2.3 eV respectively. BTBPm could not be successfully synthesized via Sarandeses reaction with either ThClPm or ThIPm. The synthesis of BTIPz-HD₂ and BEIPz-HD₂ required a lengthy preparation of precursors. Purification of BTIPz-HD₂ could not be achieved due to minimal separation on the columns. BEIPz-HD₂ awaits purification by column chromatography.

Future Work

Improvements to the synthesis of BTIPz-HD₂ and BEPIz-HD₂ could be made. If the precursor to the ring closure could be purified then the final product should be easy to isolate because the ring closure goes to nearly 100% completion. Another change could be to replace the long alkyl chains with oligoether chains; this would result in a product that was a solid instead of an oil and then purification could be achieved via recrystallization so that the electrochemistry could be performed on these two monomers. The same could be said for the synthesis of BProPm-Bu₂ in terms of using oligoether groups as opposed to alkyl groups. If this product was a solid, recrystallization may help to improve yields. BTBPm synthesis could possibly be improved by using DMF as a solvent, due to its high boiling point the reaction could be run at higher temperatures. The melting point of DMF is also low enough that lithiation could be performed at -78°C. The problem with using DMF is that its high boiling point makes removal of the solvent problematic. The purification of BEPIz-HD₂ will be attempted so that it may be studied electrochemically

APPENDIX NUCLEAR MAGNETIC RESONANCE SPECTRA

Spectrum

Page

1.	ProDOT-Bu ₂ ¹ H NMR in CD ₂ Cl ₂
2.	Product from attempted synthesis of BTBPm via Negishi ¹ HNMR in CDCl ₃ 59
3.	Product from attempted synthesis of BPPm-Bu ₂ via Negishi ¹ H NMR in
	CDCl ₃ 60
4.	BPPm-Bu ₂ synthesized via Sarandeses coupling ¹ H NMR in CDCl ₃ 61
5.	BPPm-Bu ₂ synthesized via Sarandeses coupling; ¹³ C NMR in CDCl ₃ 62
6.	ThClPm ¹ H NMR in CDCl ₃ 63
7.	ThIPm ¹ H NMR in CDCl ₃ 64
8.	Attempted synthesis of BTBPm via Sarandeses coupling ¹ H NMR in CDCl ₃ 65
9.	DEM-H ₂ ¹ H NMR in CDCl ₃
10	. DEM-HD ₂ ¹ H NMR in CDCl ₃
11	. MalCl-HD ₂ 1 H NMR in CDCl ₃
12	. MalCl-HD ₂ 13 C NMR in CDCl ₃
13	. Attempted synthesis of BTIPz-HD ₂ full spectrum ¹ H NMR in CDCl ₃ 70
14	. Attempted synthesis of BTIPz-HD ₂ zoomed in spectrum ¹ H NMR in CDCl ₃ 71







Spectrum 2. Product from attempted synthesis of BTBPm via Negishi ¹HNMR in CDCl₃






Spectrum 4. BProPm-Bu₂ synthesized via Sarandeses coupling ¹H NMR in CDCl₃



Spectrum 5. BProPm-Bu₂ synthesized via Sarandeses coupling; ¹³C NMR in CDCl₃

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Spectrum 9. DEM-H₂ ¹H NMR in CDCl₃













Spectrum 13. Attempted synthesis of BTIPz-HD₂ full spectrum ¹H NMR in CDCl₃





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